Theoretical Calculations on Diels-Alder Reactions: Case Study of Cyclopentadiene and Alkyl Acrylate

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Abstract: Diels-Alder reactions are more complex than the simple interaction between the reactants suggests and no justification can be generalized in an attempt to explain the selectivity of a given product. Therefore these reactions continue to be a challenge for high-accuracy calculations [1]. An interesting case that may exemplify the nature of this type of mechanism is the reaction between cyclopentadiene and alkyl acrylate, R = H and R = CH_3 (Figure 1) [2-5]. The simple substitution of hydrogen by a methyl group in the dienophile is responsible by the opposite predominance of the product formed.
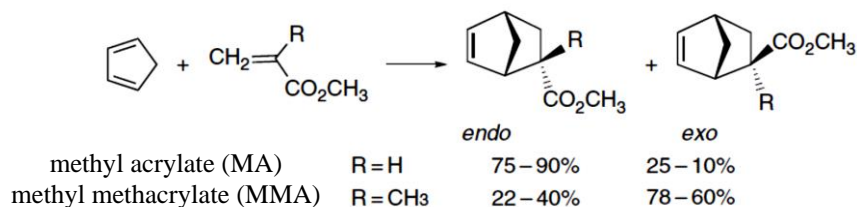
	R	endo	exo
methyl acrylate (MA)	R = H	75 − 90%	25 − 10%
methyl methacrylate (MMA)	R = CH_3	22 − 40%	78 − 60%

Figure 1. Scheme of the reaction between cyclopentadiene and alkyl acrylate.

Ruiz-López et al. [3] by using the SCRF model and ab initio calculations suggest that the polarity of the medium influences the selectivity of these particular reactions. Hondrogiannis et al. [4] say that the ratio of endo to exo products is strongly dependent on the activity of the alumina. Stefaniak et al. [5] showed that a higher stereoselectivity to the endo isomer was found in the majority of cases involving cyclopentadiene and alkyl acrylates in the presence of pyrrolidinium ionic liquids.

In this work, calculations were performed with the Gaussian 09 program, initially at the B3LYP/6-31G(d) level followed by QCISD(T) single point calculations using the same basis set. The results showed a small energy difference of ~0.5 kcal mol^{-1} between the barriers and stereoisomers formed by the reaction between Cp and MA, with both levels of theory tested. This is not enough argument to explain the experimental yield for this reaction. The transition state (TS) were characterized by a single imaginary frequency.

For the Cp and MMA reaction, it is observed a difference between barriers of 1.3 kcal mol^{-1} in favor of the path leading to the exo product. This difference decreases to 0.8 kcal mol^{-1} with QCISD(T). Finally, the TSs were submitted to the Intrinsic Reaction Coordinate (IRC) procedure at the B3LYP/6-31G(d) level of theory and the results can be seen in Figure 2.
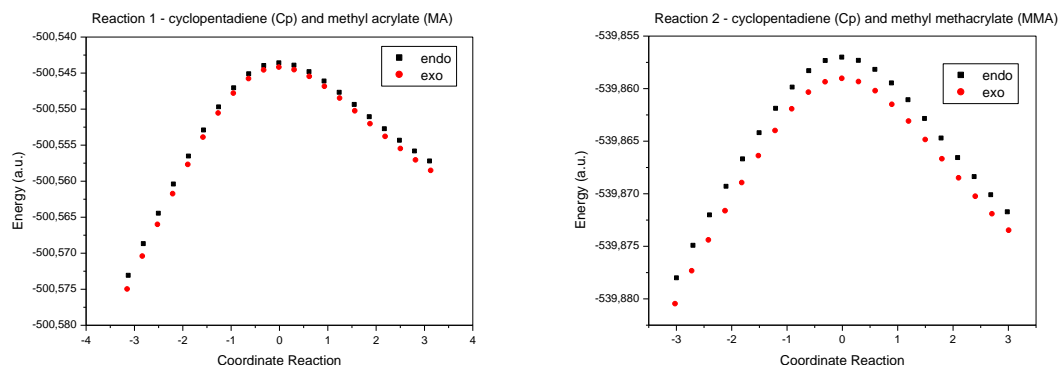
Figure 2. IRCs for the reactions between the Cp + MA (left) and Cp + MMA (right).

The energy differences below 1 kcal mol^{-1} between both barriers or products are not sufficient to justify the experimental yield of the reaction between Cp and MA. The lower barrier of the reaction between Cp and MMA for the exo path shows that the factors controlling the endo:exo selectivity changes according to specific cases, such as the reactions treated in this work where steric effects prevail. More accurate calculations are being carried out and will be presented in the meeting.

Key-words: Diels-Alder reaction, steric effects, endo/exo selectivity.

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